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Remediation of a historically Pb contaminated soil using a model natural Mn oxide waste

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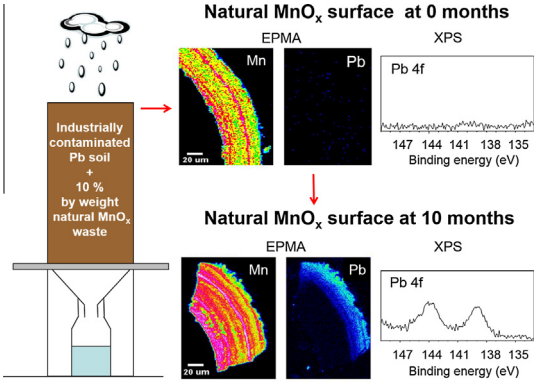
HIGHLIGHTS

- The use of a natural Mn oxide (NMO) waste for the remediation of Pb contaminated soils is reported.
- The NMO shows one of the highest Pb sorption capacities reported to date.
- Available Pb in contaminated soil effectively binds to the NMO.
- NMO addition does not perturb soil microbial communities or their function.

GRAPHICAL ABSTRACT



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ABSTRACT

A natural Mn oxide (NMO) waste was assessed as an *in situ* remediation amendment for Pb contaminated sites. The viability of this was investigated using a 10 month lysimeter trial, wherein a historically Pb contaminated soil was amended with a 10% by weight model NMO. The model NMO was found to have a large Pb adsorption capacity (q_{max} 346 ± 14 mg g^{-1}). However, due to the heterogeneous nature of the Pb contamination in the soils (3650.54–9299.79 mg kg^{-1}), no treatment related difference in Pb via geochemistry could be detected. To overcome difficulties in traditional geochemical techniques due to pollutant heterogeneity we present a new method for unequivocally proving metal sorption to *in situ* remediation amendments. The method combines two spectroscopic techniques; namely electron probe microanalysis (EPMA) and X-ray photoelectron spectroscopy (XPS). Using this we showed Pb immobilisation on NMO, which were Pb free prior to their addition to the soils. Amendment of the soil with exogenous Mn oxide had no effect on microbial functioning, nor did it perturb the composition of the dominant phyla. We conclude that NMOs show excellent potential as remediation amendments.

1. Introduction

The use of soil amendments capable of *in situ* metal immobilisation is increasingly seen as a competitive and sustainable remediation option to reduce the availability of contaminants to humans,

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plants and soil organisms. Lead (Pb) is a potentially toxic element (PTE) common in anthropogenically contaminated soils. As the environmental risk associated with Pb is related to its extractability, current remediation strategies strive to reduce its bioaccessibility and bioavailability. To date commercial remediation has focused upon solidification/stabilisation (SS) using: (i) cementitious binders, (ii) phosphate rock amendments, and (iii) lime.

In recent years alternatives to these traditional approaches have been suggested which include: fixation on clays, red mud, organic materials, zeolites and nanomaterials. However, it is well known that in soils, Pb preferentially binds to mineral oxides, in particular, Mn oxides (MnO_x) Dong et al., 2003; Wang et al., 2012. As a result, the use of MnO_x as soil amendments for Pb remediation has received heightened interest recently (Mench et al., 1994; Hettiarachchi et al., 2000). MnO_x amendments have traditionally not been viewed as a viable strategy as only expensive synthesised resources existed. Recently, a large international source of waste MnO_x (Mn mining industry by-product) has been identified (Clarke et al., 2010). In addition, waste supplies of MnO_x, such as MnO_x-coated sands are available nationally. These wastes of Mn(II)-removing clean water treatment plants which would otherwise be disposed of via landfill. Both byproducts' can be classified as a natural manganese oxide (NMO) and may provide, an additional competitive, sustainable and cost effective remediation option.

The successful sorption of Pb in aqueous systems by various types of NMO has been extensively studied in recent years (Boujelben et al., 2009; Lee et al., 2004), yet they have never been considered for soil remediation. NMO's may differ in its reactions with Pb in the complex soil environment due to variations in mineralogy, accessory elements, surface areas, presence of organic coatings and contact with available Pb (Tebo et al., 2004). In soils Pb has the potential sorb onto multiple phases such as clay minerals, organic matter and inherent Fe and MnO_x minerals. With its availability will be affected by site specific conditions, such as water infiltration rates, pH and metal speciation. Yet, research shows that MnO_x accumulate more Pb than other environmental sorbates in soils having a high affinity for the binding of this metal (McKenzie, 1980). This is supported by sequences of MnO_x sorption selectivity recurrently show a preference for Pb over other metal cations in the soil environment (Covelo et al., 2007). There is a strong scientific basis for Pb remediation by *in situ* exogenous MnO_x. Sorption of Pb to MnO_x has been shown to be irreversible via the formation of strong inner and outer sphere complexes on octahedral vacancy sites in the malleable crystal structure of MnO_x minerals (McKenzie, 1980; Villalobos et al., 2005; Manceau et al., 1992; Matocha et al., 2001). Owing to the small particles size and high specific surface areas MnO_x possess they exhibit high surface reactivity, this coupled to their low point of zero charge, which generally falls between a pH of 2 and 5 makes them potent scavengers of Pb (Gasparatos, 2012). Additionally, the ability of MnO_x to effectively immobilize Pb resulting in no risk from human ingestion has been described (Beak et al., 2007). However, others suggest the presence of Mn oxides may increase bioaccessibility (Ruby, 2004). To date no work has been carried out to determine the fate of Pb bound to natural MnO_x.

The effect of exogenous minerals and indeed remediation amendments on soil microbial function and communities has with a few exceptions (Uroz et al., 2012; Meynet et al., 2012) been poorly investigated. Evidence suggests that altering the mineral composition of a soil will have an effect upon its microbial population (Uroz et al., 2012; Carson et al., 2007). The maintenance of such populations is pertinent to the restoration of contaminated sites, principally for the protection of critical ecosystem services that enable the reuse of brownfield land. For a NMO to be effective in remediation they should not only immobilize Pb but also maintain soil microbial populations and their activities.

The success of remediation strategies is based upon statistically significant changes in bulk soil chemistry. Investigators have reported that it is often too difficult to discriminate treatment effects from remediation attempts due to heterogeneity, with studies showing up to 30-fold differences in metal concentrations in sites 1 cm apart (Becker et al., 2006). Additionally, relevant control soils are often lacking in field studies which makes analysis difficult (Giller et al., 1998). This has led to studies being carried out upon non-contaminated soils which have been spiked with metal salts allowing for bulk measurements and consequent statistical testing of contaminant behaviour. Yet, such experiments do not adequately reflect contaminant behaviour in real soils requiring remediation. Heterogeneity in contaminated sites represents a great technical challenge for environmental engineers and to date the effects of pollutant heterogeneity in historical sites has received more attention in the field of microbiology (Becker et al., 2006; Giller et al., 1998).

This study sought to examine the effectiveness of the proposed amendment using soils that had been industrially contaminated for over 80 years. Such a long contamination time represents a unique 'research soil' reflective of real world remediation challenges, harbouring realistic equilibrium rates and pollutant ageing. The aims of this paper were to determine whether a NMO waste could remediate Pb in contaminated soils under realistic remediation conditions using a model system and; determine what effect the exogenous MnO_x mineral addition had on soil microbial populations. To our knowledge this is the first investigation that uses a NMO waste as a contaminated land remediation amendment and also the first assessment of the effect of MnO_x addition on soil microbial communities. In addition, we present a new spectroscopic methodology that employs electron probe microanalysis (EPMA) and X-ray photoelectron spectroscopy (XPS) to unambiguously validate metal sorption onto *in situ* amendments in heterogeneously polluted soils.

2. Materials and methods

2.1. Model NMO waste sampling and characteristics

The model NMO was sourced from rapid gravity filter beds at the Mosswood Mn-removing water treatment works (WTW), operated by Northumbrian Water Ltd. (Co. Durham, UK, 54°51′03.9″N 1°54′00.5″W). Further details of the Mosswood WTW are given in the Supplementary Information (SI). This material was analysed at Durham University, using a low vacuum environmental SEM (JSM 5300 LV) at an accelerating voltage of 20 kV in its native state. Analysis of the specific surface area was undertaken at the Soil Research Centre, University of Reading, by N_2-BET using a Gemini 2374 v4.02.

2.2. Pb Sorption experiments

Differing concentrations of Pb(II) solutions were prepared using a standard solution (AAS TraceCERT grade, Sigma Aldrich). Triplicate experiments were conducted using a 1 g l^{-1} NMO concentration (<63 μm particle size) with 0.01 M NaCl as background electrolyte and 5 mmol 2-(N-Morpholino)ethanesulfonic acid sodium salt (MES) buffer to maintain the solution pH at 5.5. Samples were shaken at room temperature for 8 h at 150 rpm before centrifugation at 2500 g for 5 min, and filtration through a 0.2 μm filter. Solutions were acidified to 1% HNO_3 then refrigerated prior to analysis by AAS. The surface composition of dried residues was investigated by XPS (details below). The sorption data was

analysed by the Langmuir adsorption isotherm model (Langmuir, 1918).

2.3. Pb contaminated soil sampling and characteristics

Pb contaminated soils were obtained from the former St. Anthony's Lead works, a site of historical anthropogenic heavy metal pollution, located in Newcastle upon Tyne (54°57′39.7″N 1°33′10.0″W). See the SI for further details. Soils were analysed on site using a Niton field portable X-ray Florescence (XRF) analyser in order to collect samples with mean representative Pb concentrations (11,000 mg kg^{-1}, Table S1). The pH and organic carbon content of the soil was determined to be 7.44 ± 0.01 (n = 3) and 8.15 ± 0.14% (n = 3) respectively.

2.4. Model NMO-waste amendment lysimeter trial

The trial consisted of triplicate lysimeters containing the Pb contaminated soil with 0% (control) and 10% NMO-waste amendment by weight. All mixtures were placed in PTFE-lined lysimeters (30 cm × 15 cm) and placed outside for 10 months to undergo natural variations in weather. Sampling was undertaken at 0 and 10 months for geochemical, spectroscopic and microbial analyses.

2.4.1. Homogenisation of historical field contaminated and lysimeter soils

After extraction from the field site, the contaminated soil was air dried and sieved (<2 mm) before readjusting to field moisture content. The soil, water and NMO (where applicable) were mixed for 30 min in a cement mixer. Following this representative 0 month sub-samples were taken, which underwent sequential extraction. After 10 months, lysimeters were destroyed and soils homogenised via air drying and sieving prior to sampling.

2.4.2. Geochemical analysis

Geochemical analyses consisted of (i) determination of Pb fractionation by sequential extraction via the modified BCR method at 0 and 10 months (Mossop and Davidson, 2003; Quevauviller et al., 1997) and (ii) bioaccessibility testing at 10 months using the BARGE-UBM method (full details in SI) (Wragg et al., 2011). All samples were air-dried and sieved prior to analysis.

2.4.3. Spectroscopic analysis

Immobilisation of Pb onto the model NMO was determined using electron microprobe X-ray mapping and XPS via direct comparison before and after exposure to the contaminated soil. After 10 months NMO grains were visually extracted from lysimeter soils. A colourimetric test using 0.04% leucoberbelin blue (LBB, Sigma–Aldrich, UK) in 0.45 mM acetic acid was used to confirm the grains as the NMO (Krumbein and Altmann, 1973). The colourless LBB reagent changes to blue via its oxidation with Mn(IV) when present. Extracted grains were placed on filter paper. The LBB reagent was added to the sample and the presence of MnO_x was confirmed when a blue colour change was observed. As a control a synthetic MnO_2 (Sigma–Aldrich, UK) was checked for reactivity and colour change.

X-ray photoelectron spectra were obtained at the National EPSRC XPS User's Service (NEXUS) at Newcastle University, an EPSRC Mid-Range Facility using a K-Alpha XPS instrument (Thermo Scientific, East Grinstead, UK). A monochromatic Al Ka X-ray source (1486.6 eV) was used with a spot size of 200 μm diameter. A pass energy of 200 eV and step size of 1.0 eV were employed for all survey spectra. A pass energy of 40 eV and step size of 0.1 eV were used for acquisition of the high resolution spectra of the elements of interest. Peak fitting of high resolution spectra was non-quantitative and used the default parameters in Casa XPS.

Electron probe X-ray mapping was performed on a Jeol 8100 Superprobe (WDS) with an Oxford Instrument Inca system (EDS). Energy spectral data were collected in the 0–20 eV range. Mapping of O, Mn and Pb was carried out using an accelerating voltage of 15 kV, current of 2.5 mA and a beam diameter of 1 μm.

2.4.4. Microbial analysis

Molecular analysis of soil microbial communities consisted of barcoded pyrosequencing of the 16S rRNA gene (full details in SI). Determination of overall soil microbial activity included measurement of basal respiration (ISO 16072, 2002), potential nitrification rates (Hoffmann et al., 2007) and denitrification enzyme activities as in Wertz et al. (2006) with a minor modification – the use of 1% acetylene (C_2H_2) in N_2. Samples for molecular and microbial functional analysis were stored at −20 °C and 4 °C respectively.

2.5. Statistical analysis

Statistical analysis of non-pyrosequence data was conducted using SPSS 17 for windows (SPSS, Inc. Chicago, IL). Significant differences between measured parameters was analysed using one-way analysis of variance (ANOVA), followed by Tukey's HSD test, or using a two tailed independent sample t-test. Differences at $p \leqslant 0.1$ were considered statistically significant.

3. Results and discussion

3.1. Characterisation of the model NMO waste

Mn was confirmed as the major metal in the NMO (30 666.7 ± 4630.8 mg kg^{-1}, Table S1), and the pH was determined to be 8.00 ± 0.01 (n = 3). However, the NMO also contained elevated levels of Cd, Ni and Zn (Table S1). These metals are present in the source water abstracted from the Derwent reservoir which has been contaminated by influent rivers carrying treatment plant and drainage water effluents from Pb, coal and fluorspar mines (Harding and Whitton, 1978). Consequently, this NMO, and others formed in areas with activities associated with high accessory metals, would not be suitable for addition to contaminated land. Nevertheless, as the objective of this study was to determine if a NMO was capable of *in situ* Pb sorption they were deemed fit for purpose as a model. It should be noted that other sources of NMO such as mine tailing by-products only have trace levels of metals in their composition (Gasparatos, 2012).

The specific surface area of the NMO ranged from 34.4 to 44.0 $m^2\ g^{-1}$. EXAFS analyses showed that that MnO_x on the NMO was a typical amorphous hexagonal birnessite (δ-MnO_2, data not shown). SEM analysis a bimodal size distribution of particles, comprising intact coated sand grains, and smaller fragments of the MnO_x rich coatings (Fig. S1a). A typical coating is clearly laminated as a result of successional deposition during formation and is approximately 50 μm thick (Fig. 1a). The birnessite found on the surface appeared as plate-like to granular clusters ranging in diameter from 1 to 3 μm (Fig. S1b). The NMO did not display detectable levels of respiration or denitrification, however, they did produce measurable potential nitrification rates at 0.27 ± 0.04 μg NO_2-N g^{-1} dry solid h^{-1}.

XPS survey scans on triplicate NMO grains showed homogeneity in surface composition, with the major elements identified as oxygen, manganese, carbon, nitrogen and calcium (Fig. 1b). High resolution O 1s spectra showed three distinct contributions to the overall photoelectron signal characteristic of oxygen in Mn

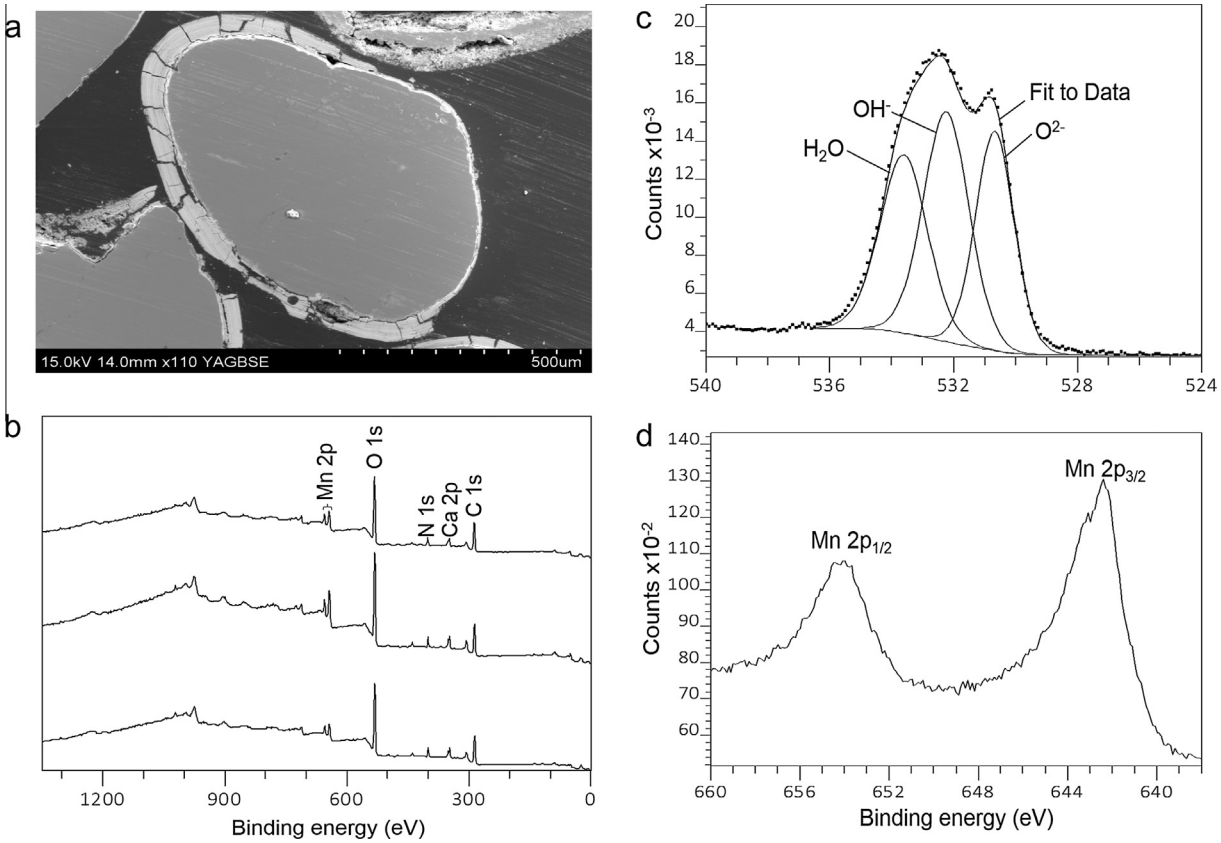

Fig. 1. (a) SEM image of cross section through a NMO grain showing the 50 μm thick birnessite coating. (b) XPS survey spectra of three distinct NMO grains. (c) An XPS high resolution O 1s spectrum. Dots represent the spectral data with the near horizontal line representing the Shirley background. The three spectral peaks which contribute to the overall peak are labelled. (d) A Mn 2p high resolution spectrum of the model NMO waste.

oxides (Nesbitt and Banerjee, 1998) (Fig. 1c). Specifically, peaks at 530, 532 and 533 eV were assigned to lattice oxygen in the MnO_x (Mn–O–Mn), hydroxide (Mn–OH), and chemisorbed or structurally bound water respectively (Nesbitt and Banerjee, 1998). Additionally, high resolution $Mn2p_{3/2}$ peak shapes were characteristic of birnessite, displaying a maxima at 642 eV, a and a visible shoulder 643 eV, (Fig. 1d), indicating that the oxidation state of the NMO is predominately 4+ (Nesbitt and Banerjee, 1998).

3.2. Pb sorption experiments

Sorption experiments were performed only to confirm if the NMO was capable of Pb immobilisation and evaluate their capacity in comparison to synthetic MnO_x and other amendments as they do not represent actual field conditions. This study was not designed to provide a mechanistic understanding of Pb sorption and bonding to MnO_x as this has already been well documented (Wang et al., 2012).

Optimum pH for Pb adsorption by the NMO was found to be 5.5 (Fig. S2) with equilibrium achieved within 1 h of contact time (data not shown). At lower pH values ionic metal adsorption onto MnO_x is inhibited due to competition between H^+ and Pb ions on available sites with a preponderance of H^+ ions bonding. As pH increases the negative charge density upon MnO_x decreases due to deprotonation with resultant increase in metal ion adsorption. Above pH 5.5 adsorption decreased. Above pH 6, Pb undergoes precipitation and adsorption percentages cannot be determined.

Sorption isotherm data (Fig. S2) was fitted to Langmuir's monolayer adsorption model and the maximum adsorption capacity (q_{max}) of the NMO was determined to be 346 ± 14 mg g^{-1} (Fig. S2). In comparison to other MnO_x amendments, the NMO was found to be 2.4–180 times larger (Table S3), comparable with a synthetic MnO_2. When compared to non-MnO_x amendments the model NMO was on average 4 times greater than alternatives such as clays, zeolites, activated carbon and organic wastes (Table S3). The q_{max} of the NMO could only be exceeded by nanomaterials, synthetically processed fertiliser plant by-products and lignin wastes indicating that that NMO are potentially one of the best Pb adsorbents discovered to date (Table S3).

3.3. Model NMO amendment lysimeter trial

3.3.1. Homogenisation of the historical field contaminated soil

Despite attempts to homogenise the contaminated soils their sequential extraction revealed the unexpected finding that the non-amended control soil had, from the outset of the experiment, a lower average total Pb concentration (4791.52 mg kg^{-1}) than the NMO-amended soil (9299.79 mg kg^{-1}). This pattern was repeated in all of the individual extracted fractions (Table S4). Such differences could not be explained by Pb addition via the NMO since this material only contained 12.0 ± 1.0 mg kg^{-1}. However, critically the 95% confidence intervals for these averages overlapped (non-amended, 3602.6 – 5980.4 and NMO amended-soil, 3578.9 – 15020.7) with the NMO-amended soil encompassing the highest and lowest values between experimental replicates (Table S4). Intriguingly these patterns were not evident for Zn and Fe (Table S4), strongly indicating that the historical point source pollution at the site had caused large spatial Pb variation which could not be overcome with the method of homogenisation employed in this study. Such problems in real Pb contaminated soils are common. Better mixing could have been achieved with pulverisation of the soil to the sub-micron scale (McBride et al.,

2011). This is wholly unreflective of an actual remediation attempt and destructive of the soil structure and consequently interactions between contaminants and amendments in the environment. As the purpose of this research was to recreate a realistic remediation attempt such homogenisation methods were not employed. In addition, results indicated that compositional heterogeneity between treatment replicates severely constrained the use of bulk geochemical data to determine the putatively smaller remediation treatment effects resulting in transfer of Pb from one soil fraction to another.

3.3.2. Geochemical analyses

In the context of this contaminant heterogeneity, and even when considering the NMO-amended soils in isolation, no significant difference could be seen in the exchangeable, reducible or oxidisable Pb fractions between 0 and 10 months ($p > 0.1$, Table S5). However, water exchangeable Pb in the NMO-amended soils showed a borderline significant decrease over time (10.74 ± 5.79 mg kg^{-1}, $p = 0.1$), but not in the control (0.76 ± 0.04 mg kg^{-1}, $p > 1$), suggesting adsorption of available Pb from pore water to the NMO over 10 months (Table S5). An analysis of the distribution of Pb in the sequential extractions showed that less than 0.2% of the total Pb was available in the water exchangeable fraction, indicating available Pb was inherently low (Table S5). Interestingly, sequential extractions also showed that over 80% of the contaminated soil Pb was consistently held in the reducible metal fraction. Indicating that Fe and Mn oxides were already the principal soil constituent controlling the mobility of Pb.

Results from Pb bioaccessibility tests at 10 months were as problematic in terms of heterogeneity. The control soils harboured significantly lower concentrations of Pb than the NMO-amended soil (Table S6). However, when bioaccessibility was calculated as a fraction, comparisons could be made (Table S6). No significant difference was found between the control and NMO-amended bioaccessible fractions ($p > 0.1$), which was not surprising due to the small decreases in water extractable Pb detected. Further discussion on the bioaccessibility results is presented in the SI.

3.3.3. Spectroscopic analyses

Due to the equivocal nature of the heterogeneous geochemical data we sought to develop a different approach to assessing *in situ* metal immobilisation on remediation amendments in contaminated soils. Further, while chemical analyses such as sequential or MnO_x only selective extracts (Tipping, 1985) can putatively identify changes in concentration of metals bound to MnO_x phases, they cannot distinguish between metal sorbed to intrinsic soil MnO_x or exogenous NMO. To avoid these limitations, we introduce a method which combines two spectroscopic techniques, electron probe X-ray mapping and XPS, to directly verify metal adsorption to NMO in a complex soil matrix.

X-ray mapping has been traditionally employed to characterise mineralogical phases in environmental matrices, and biosorption of metals on bacteria. XPS is extensively used in materials science and in analysing geological surfaces. XPS provides the semi-quantitative information on the elemental composition of surfaces and oxidation states. Here XPS was used in a non-quantitative manner to further verify the presence/absence of Pb upon the amendment surface.

Figs. 2 and 3 respectively show elemental EPMA micrographs and high resolution Pb 4f XPS spectra of a typical Pb free NMO grain that had (i) not been added to the contaminated soil and (ii) after 10 months in lysimeters. Both methods show that Pb is present and therefore immobilised on the outer layer of the NMO, which was Pb free prior to addition. It is important to note that both EPMA and XPS analysis indicate low to medium levels of Pb on the outer MnO_x surface consistent with small changes in water available Pb from the geochemical results. Further examples of NMO Pb sorption are provided in the SI (Figs. S3–S7). Due to the low intensity of XPS Pb4f spectral peaks, binding energy maxima could not be accurately determined. However, all spectra showed doublet peaks at 138 eV and 143 eV which can be assigned to Pb $4f_{7/2}$ and Pb $4f_{5/2}$ respectively. Peaks observed at 138 eV are in agreement with that reported in the literature for PbO and also Pb sorption onto MnO_x (Zou et al., 2006; Han et al., 2006), further verifying fixation of Pb onto the NMO.

When lysimeter results are considered as a whole it can be concluded that the model NMO immobilised Pb *in situ* in these industrially contaminated soils. However, levels of Pb transferred may be low as a result of: (i) the relatively short 10 month length of the trial and/or, (ii) the soil pH, and (iii) to the ability of the soil to provide Pb, which is limited by its mass transfer from minerals, sorbates and complexed forms. EMPA data (not given) show that

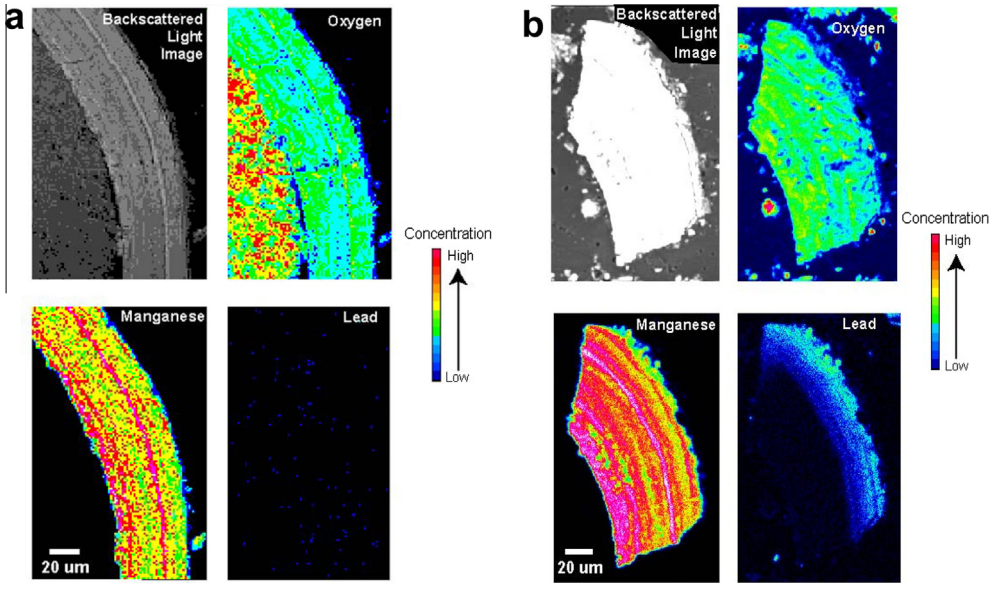

Fig. 2. Electron microprobe X-ray maps of (a) NMO not added to the Pb contaminated soil. (b) The NMO recovered after 10 months contact with the Pb contaminated soil (10% NMO amendment).

Pb in the former St. Anthony's Lead Works site prior to amendment with the NMO occurred as galena (PbS) that alters to Pb carbonate ($PbCO_3$). Lead carbonate is more soluble than PbS ($K_s = 7.40 \times 10^{-14}$ for $PbCO_3$; $K_s = 3 \times 10^{-28}$ for PbS (Clever and Johnston, 1980) and therefore have dissolved to provide aqueous Pb ions for sorption onto the NMO in higher quantities and more rapidly than PbS. In a mixed system the carbonate dissolution would likely retard sulphide dissolution based on the common ion effect, whereby Pb dissolution from the carbonate causes the solubility product of PbS to be exceeded, and hence favours Pb release from $PbCO_3$. It is important to note that these limitations are relevant to all *in situ* amendment strategies and more studies using real contaminated soils assessed over extended periods are required to assess the feasibility of novel amendments.

3.3.4. Microbial analysis

Our results suggest that addition of exogenous MnO_x does not have any direct toxicological effects on soil microbial activity. After 10 months no statistically significant difference was found between basal respiration, denitrification enzyme activity or potential nitrification rates in Pb contaminated soils with and without waste NMO ($p > 0.3$, data not shown). Bar-coded pyrosequencing of 16S rRNA genes revealed that 6 dominant bacterial phyla accounted for 93–95% of the total community in the lysimeter soil communities, and 98% of the NMO community (Fig. S8 and Table S7). However, at this phylogenetic resolution the NMO was less diverse (Tables S8 and S9) and structurally distinct from both the amended and unamended soils at 0 and 10 months (Fig. S8). At the phylum level, the *Proteobacteria*, were relatively more abundant in the NMO (78%) than in the contaminated soils (52%), interestingly the *Nitrospirae* were also 22-fold more abundant in the NMO. In contrast, the diversity in the soils was found to be 10-fold higher (Chao richness) and more even (Pielou evenness) than in the NMO regardless of time (Table S9). These data suggest that soil microorganisms were neither augmented nor perturbed by the addition of exogenous MnOx, which is consistent with the absence of any effects on measured function.

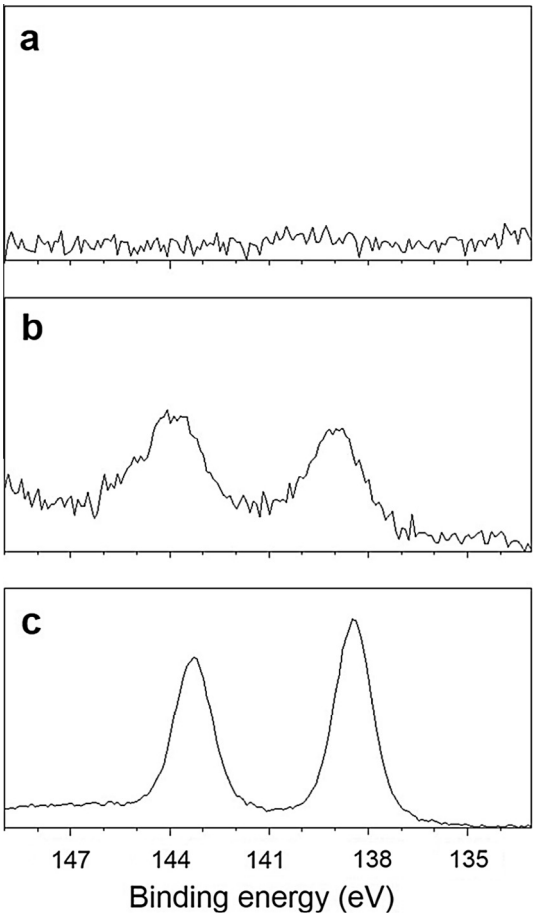

Fig. 3. High resolution Pb 4f XPS spectra showing the NMO amendment (a) 'as is' (b) after recovery from a Pb contaminated lysimeter soils (10 months) and (c) from a laboratory Pb sorption isotherm experiment as a control. Doublets characteristic of Pb can be seen at 138 eV and 143 eV which can be assigned to Pb $4f_{7/2}$ and Pb $4f_{5/2}$ respectively. Please note that peaks are smaller on spectrum (b) than on (c) due to lower concentrations of Pb available for sorption.

4. Conclusions

In the present study a model waste NMO was explored as a potential *in situ* amendment for the remediation of industrially Pb contaminated soils. Results demonstrated that the NMO is an effective Pb sorbent which are only exceeded by nanomaterials at present. Studies with field soils showed, at 10% by weight NMO amendment, no significant effect upon bulk Pb geochemistry could be detected by sequential extractions and bioaccessibility testing. This was due to large pollutant heterogeneity inherent in the solid phase of the contaminated field soils. We have developed an alternative approach to traditional geochemical methods using the spectroscopic techniques, EPMA and XPS, which unequivocally proved Pb adsorption onto the MnO_x coating of the exogenous NMO. Future work should identify uncontaminated waste NMOs such as MnO_x mine tailings (Clarke et al., 2010) which should be trailed in contaminated field soils. While the model NMO used in this study would not be suitable for application to land it could provide an excellent adsorbate for Pb removal from contaminated waters. This would provide another sustainable option for these wastes at the end of their water treatment industry life.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.05.054.

References

Beak, D.G., Basta, N.T., Scheckel, K.G., Traina, S.J., 2007. Linking solid phase speciation of Pb sequestered to birnessite to oral Pb bioaccessibility: implications for soil remediation. Environ. Sci. Technol. 42, 779–785.
Becker, J.M., Parkin, T., Nakatsu, C.H., Wilbur, J.D., Konopka, A., 2006. Bacterial activity, community structure, and centimeter-scale spatial heterogeneity in contaminated soil. Microb. Ecol. 51, 220–231.
Boujelben, N., Bouzid, J., Elouear, Z., 2009. Removal of lead(II) ions from aqueous solutions using manganese oxide-coated adsorbents: characterization and kinetic study. Adsorpt. Sci. Technol. 27, 177–191.
Carson, J.K., Rooney, D., Gleeson, D.B., Clipson, N., 2007. Altering the mineral composition of soil causes a shift in microbial community structure. FEMS Microbiol. Ecol. 61, 414–423.
Clarke, C.E., Kielar, F., Talbot, H.M., Johnson, K.L., 2010. Oxidative decolorization of acid azo dyes by a Mn oxide containing waste. Environ. Sci. Technol. 44, 1116–1122.

Clever, H.L., Johnston, F.J., 1980. The solubility of some sparingly soluble lead salts: an evaluation of the solubility in water and aqueous electrolyte solution. J. Phys. Chem. Ref. Data 9, 751–784.

Covelo, E.F., Vega, F.A., Andrade, M.L., 2007. Competitive sorption and desorption of heavy metals by individual soil components. J. Hazard. Mater. 140, 308–315.

Dong, D., Derry, L.A., Lion, L.W., 2003. Pb scavenging from a freshwater lake by Mn oxides in heterogeneous surface coating materials. Water Res. 37, 1662–1666.

Gasparatos, D., 2012. Fe–Mn concretions and nodules to sequester heavy metals in soils. In: Lichtfouse, E., Schwarzbauer, J., Robert, D. (Eds.) Environmental Chemistry for a Sustainable World, Springer Science+Business Media B.V., Dordrecht, New York, pp. 1 online resource (xix, 410).

Giller, K.E., Witter, E., McGrath, S.P., 1998. Toxicity of heavy metals to microorganisms and microbial processes in agricultural soils: a review. Soil Biol. Biochem. 30, 1389–1414.

Han, R., Zou, W., Zhang, Z., Shi, J., Yang, J., 2006. Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand: I. Characterization and kinetic study. J. Hazardous Mater. 137, 384–395.

Harding, J.P.C., Whitton, B.A., 1978. Zinc, cadmium and lead in water, sediments and submerged plants of the Derwent Reservoir Northern England. Water Res. 12, 307–316.

Hettiarachchi, G.M., Pierzynski, G.M., Ransom, M.D., 2000. In situ stabilization of soil lead using phosphorus and manganese oxide. Environ. Sci. Technol. 34, 4614–4619.

Hoffmann, H., Schloter, M., Wilke, B.M., 2007. Microscale-scale measurement of potential nitrification rates of soil aggregates. Biol. Fertil. Soils 44, 411–413.

ISO 16072, Soil quality – Laboratory methods for determination of microbial soil respiration – Section 5.5 Determination of CO_2 release using gas chromatography in a flow-through system and a static system – Subsection 5.5.4.3 Injection methods, 2002.

Krumbein, W.E., Altmann, H.J., 1973. A new method for the detection and enumeration of manganese oxidizing and reducing microorganisms. Helgoländer Meeresun. 25, 347–356.

Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40, 1361–1403.

Lee, C.I., Yang, W.F., Hsieh, C.I., 2004. Removal of copper (II) by manganese-coated sand in a liquid fluidized-bed reactor. J. Hazard. Mater. 114, 45–51.

Manceau, A., Charlet, L., Boisset, M.C., Didier, B., Spadini, L., 1992. Sorption and speciation of heavy metals on hydrous Fe and Mn oxides. From microscopic to macroscopic. Appl. Clay Sci. 7, 201–223.

Matocha, C.J., Elzinga, E.J., Sparks, D.L., 2001. Reactivity of Pb(II) at the Mn(III, IV) (oxyhydr)oxide–water interface. Environ. Sci. Technol. 35, 2967–2972.

McBride, M.B., Mathur, R.R., Baker, L.L., 2011. Chemical extractability of lead in field-contaminated soils: implications for estimating total lead. Commun. Soil Sci. Plant Anal. 42, 1581–1593.

McKenzie, R.M., 1980. The adsorption of lead and other heavy metals on oxides of manganese and iron. Austral. J. Soil Sci. 18, 61–73.

Mench, M.J., Didier, V.L., Loffler, M., Gomez, A., Masson, P., 1994. A mimicked in-situ remediation study of metal-contaminated soils with emphasis on cadmium and lead. J. Environ. Qual. 23, 58–63.

Meynet, P., Hale, S.E., Davenport, R.J., Cornelissen, G., Breedveld, G.D., Werner, D., 2012. Effect of activated carbon amendment on bacterial community structure and functions in a PAH impacted urban soil. Environ. Sci. Technol. 46, 5057–5066.

Mossop, K.F., Davidson, C.M., 2003. Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. Anal. Chim. Acta 478, 111–118.

Nesbitt, H.W., Banerjee, D., 1998. Interpretation of XPS Mn (2p) spectra of Mn oxyhydroxides and constraints on the mechanism of MnO_2 precipitation. Am. Mineral. 83, 305–315.

Quevauviller, P., Rauret, G., López-Sánchez, J.F., Rubio, R., Ure, A., Muntau, H., 1997. Certification of trace metal extractable contents in a sediment reference material (CRM 601) following a three-step sequential extraction procedure. Sci. Total Environ. 205, 223–234.

Ruby, M.V., 2004. Bioavailability of soil-borne chemicals: abiotic assessment tools. Human Ecolog. Risk Assess. 10, 647–656.

Tebo, B.M., Bargar, J.R., Clement, B.G., Dick, G.J., Murray, K.J., Parker, D., Verity, R., Webb, S.M., 2004. Biogenic manganese oxides: properties and mechanisms of formation. Annual Rev. Earth Planet. Sci. 32, 287–328.

Tipping, E., 1985. Artifacts in the use of selective chemical extraction to determine distributions of metals between oxides of manganese and iron. Anal. Chem. 57, 1944–1946.

Uroz, S., Turpault, M.P., Delaruelle, C., Mareschal, L., Pierrat, J.C., Frey-Klett, P., 2012. Minerals affect the specific diversity of forest soil bacterial communities. Geomicrobiol J. 29, 88–98.

Villalobos, M., Bargar, J., Sposito, G., 2005. Mechanisms of Pb(II) sorption on a biogenic manganese oxide. Environ. Sci. Technol. 39, 569–576.

Wang, Y., Feng, X., Villalobos, M., Tan, W., Liu, F., 2012. Sorption behavior of heavy metals on birnessite: relationship with its Mn average oxidation state and implications for types of sorption sites. Chem. Geol. 292–293, 25–34.

Wertz, S., Degrange, V., Prosser, J.I., Poly, F., Commeaux, C., Freitag, T., Guillaumaud, N., Roux, X.L., 2006. Maintenance of soil functioning following erosion of microbial diversity. Environ. Microbiol. 8, 2162–2169.

Wragg, J., Cave, M., Basta, N., Brandon, E., Casteel, S., Denys, S., Gron, C., Oomen, A., Reimer, K., Tack, K., Van de Wiele, T., 2011. An inter-laboratory trial of the unified BARGE bioaccessibility method for arsenic, cadmium and lead in soil. Sci. Total Environ. 409, 4016–4030.

Zou, W., Han, R., Chen, Z., Shi, J., Hongmin, L., 2006. Characterization and properties of manganese oxide coated zeolite as adsorbent for removal of copper(II) and lead(II) ions from solution. J. Chem. Eng. Data 51, 534–541.